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ARTICLE TYPE

Structural modulation of internal charge transfer in small molecular donors for organic solar cells

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Donor-acceptor molecules with small chain extension have been synthesized and used as active material in organic solar cells. The effect of fusion of a phenyl group on the end dicyanovinylene acceptor is discussed.

¹⁰ Organic photovoltaic cells (OPV) offer the possibility to develop lightweight and cost effective solar cells by means of low environmental impact technology. Although low band gap processable conjugated polymers remain a major class of donor materials for OPV,¹⁻⁴ the past few years have witnessed the ¹⁵ growing importance acquired by donors based on small molecules.^{5,6} Besides the obvious advantages of perfectly defined chemical structures in terms of reproducibility of synthesis, purification and performances, molecular donors allow a more straightforward analysis of structure-properties relationships than ²⁰ polydisperse polymers. In recent years this approach has generated a huge amount of work and many new classes of molecular donors have been synthesized and evaluated.⁵⁻¹⁸

The structure of efficient molecular donors generally involves a combination of donor and acceptor blocks in order to create an

²⁵ internal charge transfer (ICT) which produces at the same time an extension of the absorption spectrum towards longer wavelengths and a decrease of the HOMO level which results in an increase of the open-circuit voltage (V_{oc}) of the OPV cell.⁷ Although interesting results have been obtained with different classes of ³⁰ molecular donors⁵⁻¹⁸ such as triphenylamines,^{7,8} oligothiophenes,⁹⁻¹² squaraines,¹³ diketopyrrolopyrroles¹⁴ or borondipyrromethenes,¹⁵ these materials are in general based on

rather large molecules of high molecular weight. In this context, the question of the size of the donor molecule

³⁵ appears as an interesting problem. In fact, recent work has shown that interesting photovoltaic performances could be obtained with molecular donors of limited spatial extension and molecular weight.^{17,18} In fact, the question of the minimal size of the donor is not trivial and could have important implications regarding

40 some economic aspects of future industrial production of active materials for OPV

We report here preliminary results on small molecular donors **1** and **2** combining a triphenylamine donor block (TPA) with a dicyanovinyl thiophene electron acceptor group. In an attempt to ⁴⁵ modulate the characteristics of the ICT,⁷ the dicyanovinyl group has been fused to the thiophene by a phenyl ring (**2**). The synthesis of these compounds is described and a comparative analysis of their performances in simple OPV cells is presented.

The synthesis of compounds 1^{19} and 2 is shown in Scheme 1. ⁵⁰ A Stille coupling between the commercial bromo derivative of triphenylamine (TPA) (5) and 2-(tri-*n*-butylstannyl)thiophene gave compound 4 (52% yield) which was subsequently subjected to Vilsmeir formylation to give aldehyde 3 in 74% yield. The target compound 1 was then obtained in 75% yield by ⁵⁵ Knoevenagel condensation of 3 with malononitrile.



Scheme 1 Synthesis of compounds 1 and 2

A Stille coupling of the stannyl compound **6**, obtained by reacting bromo-TPA (**5**) with *n*-BuLi at low temperature followed ⁶⁰ by addition of Bu₃SnCl,²⁰ with the key bromo derivative **7** (see ESI) in the presence of a palladium catalyst gave the target compound **2** in 87% yield.

The UV-Vis absorption spectrum of **1** shows two maxima in the 300-400 nm region and an intense absorption band with a ⁶⁵ maximum at 501 nm assigned to an ICT band (Fig. 1).⁷ Comparison with the spectrum of **2** shows that introduction of a fused phenyl ring in the acceptor block produces a red shift of the maximum of the ICT band to 610 nm together with a decrease of its relative intensity with a *ca* twofold decrease of the molecular 70 absorption coefficient (ε) (Table 1).

Thermal analysis by DSC and TGA measured at 10° C/min under N₂ shows that the bridging of the acceptor unit in **2** leads to a significant increase of melting point (127-129°C for **1** and 24945 electrode.

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 251° C for **2**) and improves thermal stability as deduced from the decomposition temperatures determined at 5% weight loss (292°C for **1** and 334°C for **2**, see ESI).



Fig. 1 UV-Vis absorption spectra of 1 (solid line) and 2 (dotted line) in $\rm CH_2Cl_2$

The crystal structure of compound **2** shows that except for the two phenyl groups of the TPA unit, the conjugated system adopts a planar geometry, whereas the molecular packing exhibits a ¹⁰ head-to-tail arrangement as generally observed for strongly dipolar molecules^{17b,17c,18} with a distance of 3.40 Å between the planes of two neighbouring molecules (Fig. 2).



Fig. 2 Crystallographic structure of compound 2

Cyclic voltammetry performed in CH_2Cl_2 in the presence of Bu_4NPF_6 as supporting electrolyte shows that compounds are reversibly oxidized into the corresponding cation-radical with identical anodic peak potential (E_{pa}) of 1.00 V vs SCE (see ESI, 20 Fig. S4).

Table 1 UV-Vis absorption^{*a*} and cyclic voltammetric^{*b*} data for compounds 1 and 2

Compd	$\lambda_{maxICT}{}^a$ nm	\mathcal{E}_{maxICT}^{a} M ⁻¹ cm ⁻¹	${E_{pa}}^b$ V	${E_{pc}}^b$ V	E_{HOMO}^{c} eV	$e^{E_{LUMO}c}$	∆E eV	$E_g^{\ d}$ eV
1	501	33900	1.00	-1.23	-5.96	-3.79	2.17	2.03
2	610	16200	1.00	-0.80	-5.96	-4.22	1.74	1.59

^{*a*} in CH₂Cl₂; ^{*b*} 1 mM in 0.10 M Bu₄NPF₆/CH₂Cl₂, 100 mV s⁻¹, Pt working electrode, Ref. SCE; ^{*c*} using an offset of -4.99 eV vs vacuum level for

25 SCE; ^{21 d} from the low energy absorption edge of films spun-cast on glass (see ESI, Fig. S5).

Compound **1** undergoes an irreversible reduction with a cathodic peak potential E_{pc} at -1.23 V while compound **2** is ³⁰ reversibly reduced with an E_{pc} of -0.80 V. This 430 mV positive shift of E_{pc} shows that the fusion with a phenyl ring produces a

huge decrease of the LUMO level of the molecule (Table 1). This effect could be related to the stabilization of the anion-radical of **2** by aromatization of the cyclopentadiene ring.

³⁵ Compounds **1** and **2** have been used as donor material in bilayer planar heterojunction solar cells. The cells of 0.28 cm² area were fabricated using the already described procedures²⁰ (see ESI). In spite of the absence of solubilising groups, the donors were soluble enough for solution-processing. The donor layer of ⁴⁰ 35 nm thickness was spun-cast from chloroform solutions of **1** or **2** (10 mg/mL) on ITO substrates pre-coated by a 40 nm layer of PEDOT:PSS. A 30 nm layer of C₆₀ was then deposited by thermal evaporation under vacuum and the devices were completed by vacuum deposition of a 100 nm aluminium



Fig. 3 External quantum efficiency spectra of the bilayer cells based on donor 1 (solid line) and 2 (dotted line)

Fig. 3 shows the external conversion efficiency (EQE) spectra 50 of the two types of cells under monochromatic irradiation. The spectrum of the cell based on donor 1 shows a broad wave extending from 350 to 650 nm with a maximum of 45% around 530 nm. For the cell based on 2 the spectrum shows a first maximum at ca 460 nm followed by a second broad band 55 extending from 550 to ca 820 nm. The EQE spectrum is consistent with the red shifted ICT band observed in the UV-Vis spectrum of donor 2 (Fig. 1), although the relative contribution of the ICT band to the photocurrent is smaller than expected. The current density vs voltage curves recorded in the dark and under 60 simulated solar irradiation in AM 1.5 conditions are shown in Fig. 4. The cell based on donor 1 gave a short-circuit current density (J_{sc}) of 5.03 mA cm⁻² and a V_{oc} of 0.85 V. Combined with a filling factor (FF) of 43%, these data lead to a power conversion efficiency (PCE) of 2.04%. A five minutes annealing $_{65}$ at 120°C produced a substantial increase of J_{sc} and V_{oc} leading to a PCE of 2.53 % (Table 2).

The results obtained with donor **2** show that the as-fabricated cell presents the same V_{oc} of 0.85 V, as expected from the identical HOMO level, but smaller initial value of J_{sc} , *FF* and 70 *PCE*. However, a five minutes thermal treatment produces a large increase of these values with a *PCE* close to 3.00%.

To summarize we have shown that the covalent bridging of the dicyanovinyl thiophene acceptor group by a phenyl ring represents an efficient synthetic approach for engineering the ICT ⁷⁵ and the LUMO energy level of donor materials based on dipolar small donor-acceptor molecules.

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Fig. 4 Current density vs voltage curves for thermally annealed bilayer cells donor/ C_{60} (s = 0.28 cm²), in the dark (O) and under white light illumination at 90 mW cm⁻² (\bullet). Donor **1** (top), donor **2** (bottom)

 $_5$ **Table 2** Electrical characteristics of bilayer heterojunction solar cells under AM 1.5 simulated solar irradiation at 90 mW cm $^{-2}$

Compd	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}$ (V)	FF (%)	PCE (%)
1	5.03	0.85	43	2.04
1^{a}	5.77	0.92	42	2.53
2	3.57	0.85	41	1.37
2^a	5.32	0.97	52	2.97

Taking into account for the simplicity of the devices used for ¹⁰ evaluation, these preliminary results suggest that the use of C_{70} as acceptor and of more advanced technology for device fabrication can be expected to lead to higher performances. Work aiming at the extension of these ideas is now in progress and will be reported in future publications.

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- 25 characterization of new compounds. Crystallographic data, cyclic voltammetry, absorption spectroscopy, devices fabrication and thermal analysis. See DOI: 10.1039/b000000x/
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